

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-247499

(43)Date of publication of application : 06.09.1994

(51)Int.Cl.

B67D 5/54

B67D 5/02

C23C 16/44

(21)Application number : 05-054829

(71)Applicant : HOECHST JAPAN LTD

(22)Date of filing : 19.02.1993

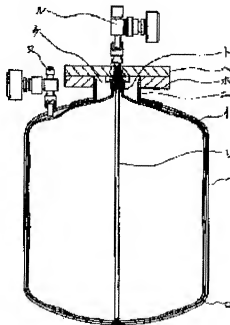
(72)Inventor : NIWA NOBUYUKI  
MASUDA TOSHIHARU

## (54) DOUBLE CONTAINER FOR LIQUID CHEMICAL AND SUPPLYING METHOD FOR LIQUID CHEMICAL INTO CVD DEVICE USING CONTAINER

### (57)Abstract:

**PURPOSE:** To obtain a stable supplying method for chemicals into a CVD(chemical vapor phase device) by penetrating a part for integrally fixing an opening part or a wall of a pressure container, and providing a valved gas introducing pipe, a valved liquid chemical introducing hole and a discharging hole for applying pressure therebetween, in a double structure of the pressure container and a film container on the inner side thereof.

**CONSTITUTION:** An interior container G formed by welding a taking-out parts formed by longitudinal two sheets made of PTFE and PFA is inserted into an external container made of pressure stainless, and composed of upper and lower end plates A, B, etc., and a chemical discharging pipe portion of a double structural container composed of an interior container fixing part H and a chemical introducing/discharging piping I is connected to a CVD device, moreover positive silicic acid ethyl is filled into the interior container from the introducing pipe side by using high purity He gas. A wafer is set in the CVD device, and the temperature is set to 400°C, moreover positive silicic acid ethyl is forcibly fed from the container. Pressure difference is provided in the piping whose aperture becomes smaller, ortho-silicic acid ethyl is vaporized and inserted into the CVD device, thereby uniform silicon oxide film can be obtained.



## CLAIMS

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[Claim(s)]

[Claim 1]It comprises dual structure with a film canister (2) of the inside which consists of an outside resisting pressure container (1) and an inactive film of shape where it became independent, respectively, Penetrate parts (3) and parts (3) which really fix an opening of these both containers (1, 2), or a wall of a resisting pressure container (1) is penetrated, A double container for liquefied chemicals which is provided with a liquefied-with valve chemicals sending-out hole (6) which penetrates a liquefied-with valve chemicals introducing hole (5) and parts (3) which penetrate a gas introducing pipe with a valve (4) for giving a pressure between a resisting pressure container (1) and a film canister (2), and parts (3) at least, and is characterized by things.

[Claim 2]A double container for liquefied chemicals which replaces with a liquefied-with valve chemicals introducing hole (5), and a liquefied-with valve chemicals sending-out hole (6) a liquefied-with valve chemicals introduction and sending-out hole (7) which penetrates parts (3), is provided with it in the double container according to claim 1, and is characterized by things.

[Claim 3]A process of introducing liquefied chemicals for CVD into an I film canister (2) through a liquefied chemicals introducing hole (5) or the introductory and sending-out hole (7) using the double container according to claim 1 or 2, \*\*) Introduce gas for feeding from a gas introducing pipe (4), and put a pressure on the outside of a film canister (2), A feeding method of liquefied chemicals to a CVD system including a process of sending out liquefied chemicals in a film canister (2) to a CVD system through a liquefied chemicals sending-out hole (6) or the introductory and sending-out hole (7).

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the feeding method of the chemicals to the CVD system using the container useful to supply and this container of chemicals to the CVD system used in the membrane formation process for electron device manufacture of a semiconductor, and LSI and others.

[0002]

[Description of the Prior Art] Various kinds of CVD (chemical vapor deposition) art is developed and put in practical use by rapid progress of the electron device in recent years for the manufacture. In the membrane formation process especially represented by formation of the interlayer insulation film in a semiconductor manufacturing process, and a conducting film, it is used dramatically.

[0003] Although it has carried out by supplying a CVD system from a high pressure cylinder by the stage film formation in semiconductor manufacture conventionally, using gaseous materials, such as silane gas, for example as a high purity chemical for CVD, Liquefied organic silicon has come to be used at ordinary temperature as a high purity chemical after that from points, such as the characteristic of the film which formed membranes, spontaneous combustion at a room temperature, and strong toxicity. In this case, liquefied organic silicon (for example, right ethyl silicate) is supplied in a reaction apparatus through the vaporizer in a CVD system at the ordinary temperature supplied to a CVD system. However, at ordinary temperature, in the case of the chemicals of a fluid, the trial which is liquefied and supplies it to a CVD system is made, and it is actually carrying out from the point that more uniform membrane formation is obtained.

[0004] When it is liquefied and supplies liquefied chemicals to a CVD system, the method of blowing inactive gas (for example, nitrogen gas, gaseous helium) into the resisting pressure container filled up with liquefied chemicals by the pressure of about one to 10 kg/cm<sup>2</sup>, and sending out liquefied chemicals is common. In this case, about the container to be used and its operation, if an example is given, it is as follows. Namely, the container has structure which attached the object for gas pouring, and two valves for liquefied chemicals extraction to the flange part in the upper part of the cylindrical cup made from stainless steel (for example, SUS304, SUS316, SUS316L), Piping which connects with the valve by the side of liquefied chemicals output port at it, and continues in a container is attached. The protector for container protection is attached to the upper part and the lower part. The container internal surface has performed the surface treatment which makes electrolytic polishing treatment representation. This container connects the valve for liquefied chemicals extraction to the CVD system side

used in the membrane formation process of a semiconductor manufacturing process, and connects the valve for gas pouring to the inactive gas (mainly  $N_2$ , helium) piping side near the manufacturing installation, and is attached. Two valves of the container after connection are changed into a "open" state, inactive gas is slushed into a container in the range of 1 - 10  $kg/cm^2$ , and the liquefied chemicals in a container are sent out to a CVD system by the pressure. After evaporating with the vaporizer in a CVD system, or after passing along the inside of piping with a liquid phase state and establishing and evaporating a pressure differential, the liquefied chemicals which were mixed with inactive gas and sent out are sent in a reaction apparatus, and are used as gas for membrane formation processes.

[0005]

[Problem(s) to be Solved by the Invention]However, in the feeding method to the above CVD systems. It happens that the inactive gas blown into the container serves as a bubble, and carries out the regurgitation in piping after penetration and chemicals are extruded by chemicals from a container in a container, and the stability of the flow of chemicals is checked (the inside of a container is sealed by the pressure of 0.1 - 0.5  $kg/cm^2$ ). This is considered to become a bubble and to appear in the stage where the pressure was eased, after the inactive gas which melted by it comes out of a container, in order to put a pressure 20 to 100 times the pressure of the inactive gas poured in for seal, when sending out chemicals. Since a (b) metal resisting pressure container is directly filled up with chemicals, the inactive gas for (\*\*) feeding for which the washing process of the container before (\*\*) product restoration for which inner surface processing of a container is needed is needed has a difficulty of \*\* which must use a high grade article in such a method.

[0006]Therefore, mixing with the chemicals [ this invention ] at the time of supply to the CVD system of chemicals and the gas for feeding is prevented, Chemicals can be supplied stably, inner surface processing of a container and selection of construction material become loose, and also it sets it as the purpose to provide the feeding method of the chemicals to the CVD system using the container for liquefied chemicals and this container which do not need to use a high grade article as gas for feeding.

[0007]

[Means for Solving the Problem]According to this invention, it comprises dual structure with a film canister (2) of the inside which consists of an outside resisting pressure container (1) and an inactive film of shape where it became independent, respectively, Penetrate parts (3) and parts (3) which really fix an opening of these both containers (1, 2), or a wall of a resisting pressure container (1) is penetrated, A gas introducing pipe with a valve (4) for giving a pressure between a resisting pressure container (1) and a film canister (2), In [ a double container for liquefied chemicals which is provided with a liquefied-with valve chemicals

sending-out hole (6) which penetrates a liquefied-with valve chemicals introducing hole (5) and parts (3) which penetrate parts (3) at least, and is characterized by things is provided, and ] this double container, A double container for liquefied chemicals which replaces with a liquefied-with valve chemicals introducing hole (5) and a liquefied-with valve chemicals sending-out hole (6) a liquefied-with valve chemicals introduction and sending-out hole (7) which penetrates parts (3), is provided with it, and is characterized by things is provided.

[0008]A process of introducing liquefied chemicals for CVD into an I film canister (2) through a liquefied chemicals introducing hole (5) or the introductory and sending-out hole (7) using the aforementioned double container according to this invention, \*\*) Introduce gas for feeding from a gas introducing pipe (4), and put a pressure on the outside of a film canister (2), A feeding method of liquefied chemicals to a CVD system including a process of sending out liquefied chemicals in a film canister (2) to a CVD system through a liquefied chemicals sending-out hole (6) or the introductory and sending-out hole (7) is provided.

[0009]A container for liquefied chemicals of this invention A resisting pressure container (it may be hereafter written as an exterior container) of the outside for chemicals feeding, Since it was considered as dual structure which consists of a film canister (it may be hereafter written as an inner package container) of the inside for chemicals restoration, by filling up an inner package container with a liquefied high purity chemical (it may only be hereafter written as a drug solution), In order that contact with a drug solution and gas for application-of-pressure feeding may be avoided, mixing with a drug solution and gas for feeding can be prevented, it may become what can supply a drug solution stably and chemicals moreover may not carry out direct contact to a wall surface of an exterior container, The necessity that gas for feeding for it becoming unnecessary to carry out special processings (for example, electrolytic polishing etc.), and selection of construction material being able to make an inner surface of a container loose, and also extruding a drug solution from a container is high purity gas is lost.

[0010]Hereafter, this invention is explained in detail, referring to an attached drawing. In [ drawing 1 is a type section figure for explaining a container of this invention, and ] drawing 1, As for parts for which 1 fixes an outside resisting pressure container (exterior container), 2 fixes an inside film canister (inner package container), and 3 really fixes an opening of the containers 1 and 2, and 4, a liquefied-with valve chemicals introducing hole and 6 are liquefied-with valve chemicals sending-out holes a gas introducing pipe with a valve, and 5. Drawing 2 is a type section figure for explaining a container of this invention of another example of composition, and it differs from a case of drawing 1 instead of the liquefied-with valve chemicals introducing hole 5 in drawing 1, and the liquefied-with valve chemicals sending-out hole 6 in that the liquefied-with valve chemicals introduction and sending-out hole 7 is formed.

[0011]A container of this invention consists of parts to which a resisting pressure container

(exterior container) of shape where it became independent, respectively, a film canister (inner package container), and they are mainly connected, and comprises dual structure which used the coupling parts (nozzle mouth) 3 inside the resisting pressure container 1, and combined the film canister 2 with it. The exterior container 1 is the shape of resisting pressure material and a cylinder system which comprised a stainless material (SUS304, SUS316, SUS316L) preferably, and can attach a protector for container protection to the upper part and/or the lower part. The container upper part can use the shape of a flanged end which can be opened and closed, and can also perform insertion into the exterior container 1 of the inner package container 2, and attachment of the coupling parts 3 in the portion. the inner package container 2 -- mainly -- a bag body-shaped inactive film -- desirable -- a plastic film. Especially consisting of a polytetrafluoroethylene (PTFE) film, the opening (drug solution output port) has composition which welded a plastic and desirable regio oralis of 4 fluoridation ethylene / product made from a perfluoroalkyl vinyl ether copolymer (PFA).

[0012]the parts 3 -- resisting pressure material -- it comprises a stainless material (SUS304, SUS316, SUS316L) preferably, and drug solution output port of the inner package container 2 is fixed to the exterior container 1. The liquefied-with valve chemicals introducing hole 5 and the liquefied-with valve chemicals sending-out hole 6 are attached to the parts 3. However, this introducing hole 5 and the sending-out hole 6 are unifiable by the liquefied-with valve chemicals introduction and sending-out hole 7, as shown in drawing 2. At this time, a valve for drug solution introduction and a valve for drug solution sending out may be separate, and a possible thing of a change an object for introduction and for sending out may be used by one. Piping (dipping tube) which connects with it and is extended to near the inner package container 2 pars basilaris ossis occipitalis can be attached to the feed port 5 and/or the delivery port 6, or the introductory and sending-out hole 7. A valve for insufflation and the gas introducing pipe 4 linked to it are attached to an exterior container shoulder or the parts 3.

[0013]In use of a container of this invention, it lets what let the liquefied chemicals introducing hole 5 pass to the inner package container 2 first, or switched the introductory and sending-out hole 7 to introduction pass, and is filled up with liquefied chemicals (drug solution) using inactive gas. As filler gas, in order to prevent penetration of gas into a drug solution, inactive gas is used, and helium gas is used especially preferably. A 0.1 - 0.5 kg/cm<sup>2</sup> grade may be sufficient as pumping pressure in this case. After being filled up with a drug solution, inactive gas is usually poured in by 0.1 - 0.5 kg/cm<sup>2</sup>, and an inner package container is fully blown up.

[0014]Next, the liquefied-with valve chemicals sending-out hole 6 or the introductory and sending-out hole 7 is connected to a CVD system used in a film production process of a semiconductor manufacturing process, and the gas introducing pipe 4 with a valve is connected to gas piping for feeding near the manufacturing installation. In order that gas for feeding used may not contact a drug solution, a kind in particular is not limited, but since it is

[0015]When a dipping tube extended to near the inner package container 2 pars basilaris ossis occipitalis is connected to the liquefied chemicals sending-out hole 6 or the introductory and sending-out hole 7, after all the drug solutions are sent out at the time of feeding of a drug solution, gas with which the inner package container 2 upper part was filled up beforehand may be sent out to a CVD system. Therefore, it is necessary to stop feeding, leaving a drug solution in this case in this side where gas is sent out by controlling a residue of a drug solution as usual. On the other hand, since a drug solution is sent out after gas of the upper part in the inner package container 2 is first sent out altogether at the time of feeding of a drug solution when not connecting a dipping tube to the liquefied chemicals sending-out hole 6 or the introductory and sending-out hole 7, all drug solutions in the inner package container 2 can be exhausted.

[0017]

[0018]The double container for chemicals of this invention which consists of the example 1 following members forming was assembled. The section structure is shown in drawing 3.

1) Main part Cylindrical shape (phi313xH433)

Panel (upper and lower sides) [I in drawing 3, RO] + Welding structure of idiosoma Ha in [drawing 3: Thickness 3mm]

2) The neck part for flange inner package container insertion [NI in drawing 3]

Lower flange[HO in drawing 3]

Upper flange (valve attachment for solution extraction) [HE in drawing 3]

**\*\* Inner package container (resin made container) : now technology company make [TO in drawing 3]**

Construction material Main part: PTFE takeoff connection :P Shape which welded the perimeter for the end of the sheet made from PTFE of two sheets of FA rectangular form (520x570), and welded [ of the longitudinal direction upper part ] the takeoff connection made from PFA is carried out.

**\*\* Coupling parts : shape It comprises the following two members.**

1) Inner package container fixing component : construction material SUS316L [CHI in drawing 3]

It comprises two members which fix the outside and the inside of a takeoff connection made from PFA of a resin made container.

2) Piping for drug solution introduction and sending out (1/4-inch piping)

Construction material SUS316L [Li in drawing 3]

**\*\* The valve for gas charging : made in FUJI Kyn [NU in drawing 3]**

Metal diaphragm valve (for 1/4 inches)

**\*\* The valve for drug solution introduction and sending out : made in FUJI Kyn [RU in drawing 3]**

Metal diaphragm valve (for 1/4 inches)

[0019]It is a CVD system about the flow pipe side of the drug solution introduction and flow pipe of said container. [kind name : Concept-One (made in Japanese Novellus Systems), Type: It connected with plasma-CVD] and the right ethyl silicate (it is henceforth written as TEOS) was filled up with the pressure  $0.1 - 0.5 \text{ kg/cm}^2$  into the inner package container from the introducing pipe side of a drug solution introduction and flow pipe using high grade helium gas. High grade helium gas was further poured in by the pressure  $0.1 - 0.5 \text{ kg/cm}^2$  after TEOS restoration, and the inner package container was fully blown up.

[0020]The wafer with a size of 6 inches was set in the CVD system, and wafer temperature was set as 400 \*\*. Next, TEOS of the flow of 1 - 20 ml/min was fed from the container by the pressure of  $1 - 10 \text{ kg/cm}^2$  using  $\text{N}_2$  gas. Then, when established the pressure differential for piping (100-300 micrometers) which becomes small [ a caliber ], and TEOS was made to evaporate and having been inserted in the CVD system, the uniform silicon oxide film was obtained. The uniform silicon oxide film was altogether obtained until it stopped feeding when



the residue of the drug solution was set to about 100 ml so that the gas with which the inner package container upper part was filled up beforehand might not be sent out.

[0021]The lead pipe for insufflation with a valve and the drug solution introduction and flow pipe with a valve were attached to the upper flange of the single container which consists of an exterior container, and the same material and the stainless steel container (a container internal surface is the electrolytic-polishing-treatment construction) of the same size which were used in comparative example 1 Example 1, and it connected with inactive gas piping and a CVD system.

[0022]Said two valves of the container after connection were changed into the "open" state, inactive gas was slushed into the container in the range of 1 - 10 kg/cm<sup>2</sup>, and the drug solution in a container was sent out to the CVD system by the pressure. The drug solution which was mixed with inactive gas and sent out was evaporated like Example 1, and was introduced into the CVD system. The CVD system, the processing condition, and the processing state are the same as Example 1. As a result, owing to inactive gas having melted into TEOS, since the fluid mass flow meter which performs a flow control generated the projection phenomenon (breathing phenomenon) by the contamination of gas and fixed supply of TEOS was not completed, membraneous quality became uneven by change of the flow into a reaction vessel.

[0023]The container which removed the dipping tube connected to the drug solution introduction and sending-out hole from the double container used in example 2 Example 1 is used, and it is as a CVD system. [Kind name :P recision-5000 (made by Applied Materials), Type: The feeding TEOS was sent into the evaporator in not piping that becomes small [ a caliber ] but a CVD system, using plasma-CVD], and except having made it evaporate applying it, when the CVD film was formed like Example 1, the uniform silicon oxide film was obtained. It continued feeding until the residue of the drug solution was set to about 0 ml, but the uniform silicon oxide film was obtained altogether.

[0024]As comparative example 2 CVD system [Kind name :P recision-5000 (made by Applied Materials), Type: The feeding TEOS was sent into the evaporator in not piping that becomes small [ a caliber ] but a CVD system, using plasma-CVD], and the CVD film was formed like the comparative example 1 except having made it evaporate applying it. As a result, since the concentration of the mixed solution of TEOS and inactive gas which that inactive gas melted into TEOS sent into the vaporizer owing to was uneven, concentration control of TEOS was not completed, but the unreacted intermediate product and the reaction intermediate product were formed by the reaction vessel, and thickness became uneven.

[0025]

[Effect of the Invention]The double container for liquefied chemicals of claims 1 and 2, The parts which comprise dual structure of an outside resisting pressure container and an inside

film canister, and really fix the opening of this container, Between a resisting pressure container and a film canister. Have at least the introductory and sending-out hole which unified the sending-out hole for sending out liquefied chemicals to the exterior from the inside of the introducing hole for introducing the gas introducing pipe with a valve and liquefied chemicals for giving a pressure into a film canister, and this container, or them, and from things.

According to the feeding method of the chemicals to the CVD system of claim 3 which uses this double container, the following effects which stood high are done so.

[0026]\*\* By filling up an inner package container with a drug solution, since contact with a drug solution and the gas for feeding is avoided, mixing with a drug solution and the gas for feeding is lost, and generating of the bubble of a under [ piping ] can be prevented. Therefore, the stable flow of a drug solution is secured and formation of a uniform CVD film is attained.

\*\* Since the gas for drug solution feeding does not contact a drug solution, the existing gas of low purity can be used as gas for feeding.

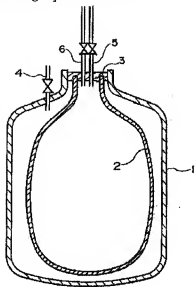
\*\* Since an exterior container internal surface and a drug solution do not contact, it becomes unnecessary to carry out special polish to the inner surface of an exterior container, and selection of container construction material also becomes loose.

\*\* By making an inner package container washing or throwing away, the cleaning cost in the exterior container after use is mitigable.

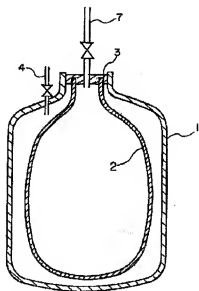
[Translation done.]

## DRAWINGS

[Drawing 1]



[Drawing 2]



[Drawing 3]

